ADMINISTRATIVE INFORMATION

1.	**Project Name:**	Thermochemical Models and Databases For High-Temperature Materials Processing and Corrosion
2.	**Lead Organization:**	Sandia National Laboratories Mail Stop 9291 Livermore, CA 94551-0969 Oak Ridge National Laboratory P. O. Box 2008 Oak Ridge, TN 37831-6063
3.	**Principal Investigator:**	Mark D. Allendorf (925)294-2895; fax (925)294-3282 mdallen@sandia.gov Theodore M. Besmann (865)574io-6852; fax (865)574-6918 tmb@ornl.gov
4.	**Project Partners:**	Advisory Board: Dr. C. Edward Ekert, Apogee Technology, Inc. Dr. Amul Gupta, Monafrax Dr. Randy John, Shell Oil Dr. Ellen Meeks, Reaction Design Dr. Dilip Patel, RHI Refractories Dr. Pavol Pranda, American Air Liquide Dr. Angel Sanjurjo, SRI International Mr. W. B. A. Sharp, MeadWestvaco Corporation Dr. Ryan Smith, Atofina Mr. John Sopko, PPG Industries Dr. David Strickler, Pilkington-LOF
5.	**Date Project Initiated:**	10/1/2001. Currently in project year 4
6.	**Expected Completion Date:**	9/30/2006

PROJECT RATIONALE AND STRATEGY

7. **Project Objective:** (Please provide 1-2 sentences describing the objective of this project.)

The objective of this project is to develop computational approaches and models for the generation of thermodynamic data required to simulate high-temperature industrial processes, and to make these data widely available to industry users through a convenient, no-cost web-accessible database. Data relevant to the manufacturing, use, and stability of refractory materials are of particular interest.

8. **Technical Barrier(s) Being Addressed:**

Efficient use of energy and raw materials at high temperatures, minimization of waste, and elimination of corrosion are intimately linked to process thermodynamics. Unfortunately, thermodynamic data for gas- and condensed-phase species needed to develop even rudimentary models of industrial processes such as glass manufacturing, metals processing, catalysis, refractory corrosion, and coating formation are often unavailable or inaccurate. Experimental efforts worldwide to generate needed data are at an all-time low due to lack of funding and the time- and cost-intensive nature of such efforts.

9. **Project Pathway:**

The approach employed in this project is to use computational methods to predict thermodynamic data and then to make these available in a user-friendly format via a web-based database. Computational methods developed over the past 20 years for predicting thermodynamic properties have demonstrated their ability to generate data sufficiently accurate for process modeling efforts. In particular, quantum-chemistry methods can now provide heats of formation for gas-phase species that are typically accurate to 2 – 3 kcal mol^{-1}. Similarly, methods for modeling condensed-phase systems, in particular amorphous and glassy phases/melts allow accurate reproduction phase diagrams and activities. Amorphous and crystalline phases formed when high-temperature water and/or oxygen react with refractories and metals them become predictable. We are using these methods, which have been under development in our laboratories prior to this project, to obtain data for chemical systems of particular relevance to industrial processes and the use of refractories in those processes. Initial efforts focused on chemistries containing main-group elements such as boron, aluminum, silicon, and tin, since these are the most-common components of refractory materials. Current efforts are focused on systems containing transition metals such as iron, chromium, and manganese, all of which are routinely used in high-temperature manufacturing, and are developing theoretical approaches capable of accurately modeling these systems. All data are provided via the web to users free of charge. Data are provided in formats compatible with standard software used to model high-temperature reacting systems, such as CHEMKIN and FactSage. The site also provides detailed information concerning the calculations and useful references.

10. **Critical Metrics:** (Please describe the application-specific metric(s) (i.e., metrics in the end-use industrial process) that will be used to determine the success of the project.)

- Generation of condensed-phase thermodynamic models capable of simulating the thermochemistry of all major refractory systems and their typical corrosion modes by oxygen, steam, and halogens.
- Generation of gas-phase data for main-group and transition-metal species relevant to refractory corrosion, including oxides and halides of the elements B, C, Ca, Al, Si, Sn, Ti, Fe, Cr, and Mn.
- Production of an on-line database that presents all of the data generated within the project in a user-friendly format suitable for immediate use by industry.

PROJECT PLANS AND PROGRESS

11. **Past Accomplishments:**

Task 1 Thermodynamic modeling of condensed-phase systems

- A database was developed that now contains Na-Ca-Al-Cr-B-Si-O, which will be of particular importance for alumina-chromia refractories typically used in gasifiers, combustors, and steel production.
- A database for the system Na-Al-Fe-B-Si-O has been developed that will allow calculations of interest in general refractory corrosion in the glass and aluminum industries.

- Lithium addition to the base liquid system Na-Al-B-Si-O has been partially completed and will be of importance for issues in aluminum smelting where lithium is an important additive to the melt.

<u>Task 2 Prediction of high-temperature thermochemistry of gas-phase species</u>

- Thermodynamic data for fluorides and chlorides of manganese, chromium, and iron were predicted (needed for modeling production and corrosion of these metals and/or refractories containing them).
- Thermodynamic data for key gas-phase species involved in the high-temperature corrosion, oxidation, and hydrolysis of chromium-containing alloys and refractories (used in black-liquor gasifiers and glass furnaces) were calculated.
- Experiments at NASA/Glenn Research Center were completed to validate computational approaches to predicting thermochemistry for chromium oxides.
- Thermodynamic functions for selected oxides and hydroxides of alkali metals (Li, Na, K) and alkaline earths (Be, Mg, Ca) were obtained (these are relevant to modeling impurity removal in aluminum melts and corrosion in glass furnaces and pulp/paper operations).
- Thermodynamic calculations for indium and antimony hydroxides (needed to model glass melts and the deposition of coatings on float glass) are complete.
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<u>Task 3 Database development</u>

- *Industry of the Future web pages added.* Web pages containing thermodynamic data files and documentation for specific problems within the glass, forest products, and aluminum industries were added to facilitate access to the data.
- *New data uploaded to the web site.* chlorides and fluorides of chromium, manganese, and iron (12 compounds); tin oxides and hydroxides (35 compounds); indium and antimony compounds (95 compounds); Li, Na, K species (6 compounds); Be, Mg, Ca species (6 compounds).
- *New phase equilibrium calculator.* A web version of the Equilib program that is part of the FactSage suite of thermodynamic modeling is now available on the site. This is a versatile equilibrium calculator that can model solutions or glasses, stoichiometric compounds condensed phases, and gases.
- *CHEMKIN equilibrium calculator now online*. An interactive version of Reaction Design's EQUIL software, developed for modeling combustion and other high-temperature gas-phase processes, is now available on the web site.
- *CHEMKIN-FactSage data converter complete*. Software that converts thermodynamic data in CHEMKIN format to FactSage format is now operational, allowing users a choice depending on which thermodynamic modeling code they prefer.
- Updated condensed-phase models for generalized refractory corrosion are now available on the web site, including models tailored for specific problems in the glass, aluminum, and forest products industries.

Future Plans:

Date	Milestone/Deliverable	Partner Activities
9/1/05	Request Advisory Board input on final-year activities relevant to specific Industries of the Future	Advisory Board review web site and provide feedback
12/31/05	Complete additions to gas-phase database for NOx prediction	
3/31/06	Complete web pages for chemicals and petroleum refining IOFs	
6/30/06	Complete calculations for gas-phase Ti, Cr, Mn, and Fe species relevant to aluminum and forest products	

	IOFs. Upload data to web	
9/30/06	Complete web pages for steel, metals casting, and mining IOFs	

12. **Project Changes:**

No changes in project scope, approach, or schedule occurred during the past year.

13. Commercialization Potential, Plans, and Activities:

Thermochemical data for gas-phase and condensed compounds are essential for predicting the thermal and chemical stability of materials used in high-temperature and/or corrosive industrial environments. Thus, such data are expected to be of wide interest to companies involved in glass melting, chemicals production, metals refining, and pulp/paper processing. The product of this research is the data obtained from high-level computations, which is the only practical means today of obtaining this information. These data are being made available free of charge through an interactive web site developed by this project. This year, we initiated development of industry-specific web pages to make it easier for users to relate these data to problems they must address. To alert potential users to this resource, we are widely advertising it through both electronic and print-media, and by linking where possible to related web sites. We developed a brochure to distribute at conferences attended by potential users. This document was also being distributed by mail.

14. **Patents, Publications, Presentations:**

- T. M. Besmann, N. S. Kulkarni, and K. E. Spear "Thermochemical Analysis and Modeling of the Al_2O_3-Cr_2O_3, Cr_2O_3-SiO_2, and Al_2O_3-Cr_2O_3-SiO_2 Systems Relevant to Refractories," *Acta Materialia*, submitted 2005.
- K. E. Spear, T. M. Besmann, M. D. Allendorf "Modeling the limiting equilibrium behavior of chemically complex oxide glass solutions," in E. Opila et al. Eds, *High Temperature Corrosion and Materials Chemistry V*, The Electrochemical Society Proceedings Series, in press, 2005.
- M. B. Nielsen, M. D. Allendorf "High-level ab initio thermochemical data for halides of chromium, manganese, and iron," *J. Physical Chemistry A*, **109**, 928-933 (2004).
- T. M. Besmann, N. S. Kulkarni, K. E. Spear, J. D. Vienna, M. D. Allendorf "Modified Associate Species Approach To Phase Equilibria Prediction For Oxide Glass Systems," *Ceramic Transactions*; 2005; v.170, p.81-89
- M. D. Allendorf, C. F. Melius "BAC-MP4 Predictions of Thermochemistry for Gas-Phase Tin Compounds in the Sn-H-C-Cl System," *J. Phys. Chem. A.*, in press 2005.
- M. D. Allendorf, A. M. B. van Mol, "Gas-Phase Thermochemistry and Mechanism of Organometallic Tin Oxide Precursors," *Topics in Organometallic Chem*, in press 2005.
- "Thermodynamics Resource: An Online Database for Scientists and Engineers," T. M. Besmann, M. D. Allendorf, and N. Kulkarni. Poster, High Temperature Materials Gordon Conference, July, 2004.
- M. D. Allendorf, T. M. Besmann et al. "Quantum Chemistry, the Web, and You: Using Computers to Generate a Really Useful Thermodynamic Database" presented at the CHEMKIN workshop, *Int. Comb. Symp.* July 25, 2004.
- A. J. Skulan, M. D. Allendorf "BAC-MP4 Predictions of Thermochemistry for Gas-Phase Indium Compounds in the In-H-C-O-Cl System," submitted to *J. Phys. Chem. A*, 2005.
- A. J. Skulan, M. D. Allendorf "BAC-MP4 Predictions of Thermochemistry for Gas-Phase Antimony Compounds in the Sb-H-C-O-Cl System," submitted to *J. Phys. Chem. A*, 2005.